

GAS PHASE SYNTHESIS OF NANOPARTICLES IN A MULTI-ELEMENT DIFFUSION FLAME BURNER

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. provisional application
5 Serial No. 60/396,784, filed July 17, 2002.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention pertains to the synthesis of nanoparticles in a
one-dimensional combustion environment employing non-premixed combustion
10 gases.

2. Background Art

Particles have been synthesized in a combustion environment
employing such techniques as flame spray pyrolysis and like synthetic methods. For
example, silica and titania particles have been produced for many years by high
15 temperature flame hydrolysis of hydrolysis-prone precursors such as silicon
tetrachloride and titanium tetrachloride. However, even minor amounts of
impurities have been known to affect the process, for example the presence of
methyltrichlorosilane in silicon tetrachloride. The particle sizes produced by such
methods as well as their degree of agglomeration span a relatively wide range, and
20 particles in the low nanosize range are difficult to obtain. Furthermore, the nature
of the particles themselves, *i.e.* crystallinity, crystalline phase, and amorphous
character, can vary widely, as can also their degree of agglomeration and chemical
composition.

Nanoparticles which have a more controlled chemical structure,
25 particle size, morphology, etc., are highly desired for use in numerous fields.

However, typical high temperature syntheses do not lend themselves to the production of well defined products.

5 For example, tin dioxide (SnO_2) is used in many applications on account of its electrical, optical, and mechanical properties, particularly as the active element in gas sensors, and in low emissivity architectural glass, solar cells, liquid crystal displays, and photodetectors. Tin monoxide (SnO) has found applications in gas sensing applications and as anodes in lithium-ion cells.

10 The performance of both tin oxides has been shown to be directly related to particle size and chemical composition, and thus the synthetic route used to produce these substances is of paramount importance. For example, SnO_2 sensor performance, *e.g.*, stability, sensitivity, selectivity, etc., has shown considerable improvement when particles of reduced size are used in such applications, particularly with mean particle sizes less than 10 nm. Sensors employing doped SnO_2 with particle sizes in the range of 15-50 nm have also shown improvement
15 over comparable sensors with larger particle sizes, and SnO performance in power cell anodes is likewise considerably enhanced with reduced particle size.

Nanosized tin (0) is also of considerable interest, particularly in lithium-ion battery anodes, where lower particle sizes reduce permanent loss of capacity due to decomposition upon initial charging. In many studies, tin particles
20 have been on the order of 100-400 nm in size or larger.

Tin oxides can be generated using a variety of synthesis techniques including sol gel processing, chemical vapor deposition, sputtering methods, flame synthesis, gas phase condensation and mechanochemical processing. Pure tin nanopowders with particles ~ 100 nm or less in size can be produced by reductive
25 precipitation. Commercial production of SnO_2 powders typically uses a sol-gel technique. Sol-gel processing of metal oxides creates agglomerated particles with irregular particle morphologies and can lead to chlorine contamination of the powders because of the chloride particle precursors used (*e.g.* SnCl_4 , PtCl_4 , etc.). A new synthesis method based on combustion of readily available compounds such

as tetramethyl tin (TMT, $\text{Sn}(\text{CH}_3)_4$) that can be used to generate crystalline nanoparticles of any of these three important materials: Sn, SnO or SnO_2 , is desirable.

Metals and metal oxides of metals other than tin are also desirable for many uses. In numerous applications, nanosized particles, particularly those with low nanosize particles, *i.e.*, sizes below 50-70 nm, have been shown to behave quantitatively different than larger particles. However, it is difficult to obtain small particles of uniform composition, particularly particles of zero valent metals or metal oxides or other oxidized species (chlorides, oxychlorides, etc.) with oxidation states lower than those ordinarily encountered, *i.e.*, SnO in the case of the tin oxides, SiO or GeO in the case of silicon and germanium, etc.

Combustion synthesis has been employed to produce oxidized metal particles, particularly those with higher oxidation states, by “combusting” in an oxidant-rich environment. The oxidant may be oxygen, preferably supplied as the pure gas, or air (especially if nitrides can be tolerated), chlorine, fluorine, etc. However, lower oxidation states and particularly the metals themselves have not been routinely obtainable by such techniques, particularly in reproducible form. K. Brezinsky, “Gas Phase Combustion Synthesis of Materials,” TWENTY-SIXTH SYMPOSIUM (INTERNATIONAL) ON COMBUSTION, THE COMBUSTION INSTITUTE, pp. 1805-1816 (1996) discussed the mechanisms involved in a variety of gas phase syntheses of refractory solids, including silicon nitride (Si_3N_4) and silicon oxides prepared from silicon tetrachloride in a flame of ethene and oxygen. However, the products appear not to be tightly controlled stoichiometrically.

S.E. Pratsinis, “Flame Aerosol Synthesis of Ceramic Powder,” PROG. ENERGY COMBUST. SCI., v. 24, pp. 197-219 (1988) discusses flame combustion synthesis of SiO_2 , TiO_2 , and Al_2O_3 powders, and summarizes prior work in this area. However, the particle sizes are relatively large, *i.e.*, about 500 nm, and Pratsinis documents the variability of product with varying flame quality, temperature, and configuration. No synthesis of zero valent metal powders or powders of low or intermediate oxidation states is reported.

It would be desirable to provide a combustion synthetic method for the production of nanoparticles which is capable of robust, sustained operation; which is capable of producing particles in the low nanosize range; which reproducibly produces particles of defined stoichiometry and structure, and which
5 is capable, when applicable, of producing particles with zero valent and/or low oxidation states as well as the thermodynamically-favored higher oxidation states.

SUMMARY OF THE INVENTION

The present inventors have discovered that synthesis of nanoparticles of a wide variety of metal and metal oxide content can be accomplished in a well
10 controlled manner by combusting a volatile nanoparticle precursor within a flame front generated by a non-premixed, multi-element diffusion flame burner which is characterized by a one-dimensional flame front. By adjusting the oxidizing/reducing character of the primary burner flame by its stoichiometry, some single precursors may be used to generate metal nanoparticles, oxide nanoparticles, or various
15 combinations of metal, oxide, and mixed oxide nanoparticles.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 illustrates a cutaway side view of a MEDFB with the number of passageways reduced for clarity;

FIGURE 2 illustrates a portion of the top surface of a MEDFB from
20 above, illustrating one arrangement of combustible gas, combusting gas, and precursor passageways;

FIGURE 3 illustrates one set of temperature profiles, or isotherms, obtained from a 2.54 x 2.54 cm MEDFB;

FIGURE 4 illustrates the temperature along one axial direction
25 orthogonal to the MEDFB surface;

FIGURE 5 illustrates the effects of combustible gas/combusting gas stoichiometry on flame temperature;

FIGURE 6 illustrates a particle size distribution of SiO_2 particles which may be obtained by the process of the subject invention;

5 FIGURE 7 illustrates variation in particle sizes obtainable at different heights above the burner surface;

FIGURE 8 illustrates the characteristic times for silica particle growth mechanisms;

10 FIGURE 9 illustrates particle size distribution obtained by combustion of tetramethyl tin;

FIGURE 10 illustrates calculated species profiles for the primary flame system for typical stiochiometric combustion conditions;

15 FIGURE 11 illustrates equilibrium calculation results of the distribution of Sn in the combustion products $\text{H}_2/\text{O}_2/\text{Sn}(\text{CH}_3)_4/\text{Ar}$ flames for $T_{\text{ad}} \cong 1000 \text{ K}$; and

FIGURE 12 illustrates equilibrium calculation results of the distribution of Sn in the combustion products of $\text{H}_2/\text{O}_2/\text{Sn}(\text{CH}_3)_4/\text{Ar}$ flames for $T_{\text{ad}} \cong 2000 \text{ K}$.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 The precursor source may be any liquid or gaseous source, which may also include particulates, particularly liquid microdroplets, which is capable of being fed to a precursor source inlet of a non-premixed multi-element diffusion flame burner ("MEDFB") in gaseous or highly dispersed form. It is preferred that the precursor be a volatilizable liquid or a gas, in order that the concentration may

be adjusted by dilution with a gas such as argon or nitrogen, or supplied as a concentrated stream, as desired. In some cases, the gas used for dilution may itself be a combustible gas such as hydrogen, methane, etc., or an oxidizing gas such as oxygen. Most preferably a gas inert with respect to the precursor is used.

5 Preferred precursors include volatile metal compounds such as, but not limited to, metal alkyls, metal olefin complexes, metal hydrides, metal halides, metal alkoxides, metal formates, acetates, oxalates, and esters generally, metal glycolates, metal glycolato alkoxides, complexes of metals with hydroxyalkyl amines, etc. Essentially all metal compounds which can be oxidized, nitrided,
10 hydrolyzed, or otherwise reacted in a high temperature flame environment may be used. All such compounds useful in the present process are termed "particle precursors."

The metals of principle interest are those of the main groups 3 to 5 of the periodic table of the elements, the transition metals, and the "inner transition
15 metals," *i.e.* lanthanides and actinides. "Metals" as used herein includes those commonly referred to as semi-metals, including but not limited to boron, germanium, silicon, arsenic, tellurium, etc. Metals of Groups 1 and 2 may also be used, generally in conjunction with a further metal from one of the aforementioned groups. Non-metal compounds such as those of phosphorous may also be used
20 when a metal is used, *e.g.* to prepare mixed oxides or as dopants. In many cases, a predominant metal compound such as a tin or silicon compound is used, in conjunction with a minor amount of another metal, particularly a transition or inner-transition metal as a dopant, to provide doped particles with unusual optical, magnetic, or electrical properties. Some preferred metals include silicon, titanium,
25 zirconium, aluminum, gold, silver, platinum and tin.

By "combusted products" of a metal precursor is meant a metal-containing particle product obtained in the flame of a MEDFB from the particle precursor. The combusted product may be a zero valent metal, an oxide or hydroxide thereof, a carbide, boride, phosphide, nitride or other species, or mixture

thereof. Preferred products are zero valent metals, metal oxides, or metal nitrides, more preferably zero valent metals and/or metal oxides.

5 The combustible gas employed is any gas which is capable of being oxidized under the flame conditions. Hydrogen gas is preferred in many applications, but methane, ethane, ethene, propane, propene, acetylene and other hydrocarbons, or hydrocarbonoxy compounds such as lower alcohols, ketones, etc. may also be used. Combinations of gases, particularly combinations of hydrogen and lower alkanes may be useful in many applications.

10 The combusting gas is preferably oxygen, but in some cases, other gases such as chlorine, fluorine, nitrogen, etc., may also be used, either alone or in combination with oxygen. Ozone is also useful. Air may be used as a source of oxygen, particularly when the precursor, the reaction conditions, or the product requirements either prohibit the formation of nitrides, or in the case of the product, where nitrides can be tolerated or are the desired product.

15 The combustion takes place employing a non-premixed multi-element diffusion flame burner ("MEDFB"). A MEDFB consists of a preferably planar array of closely spaced passages for separate introduction of combustible gas and combusting gas. In general, the passageways are separated only by walls therebetween which are of sufficient thickness to maintain the mechanical integrity
20 of the device in view of the high temperatures which can be expected.

 The passageways of the MEDFB preferably have regular geometric cross-sections, for example circular, triangular, square, hexagonal, etc. Hexagonal cells are preferred. In general, the combustible gas passages are manifolded together as are the combusting gas passages, although a plurality of groups of
25 manifolded passageways, and even non-manifolded (individually supplied) passageways are also possible. In large devices, it may be preferable or even necessary to provide for a multiplicity of burner arrays which can be stacked parallel to each other to provide a large burner surface.

The combusting gas and combustible gas passageways are configured in a regular array across the surface of the burner such that combustible gas passageways are surrounded by combusting gas passageways, or combusting gas passageways are surrounded by combustible gas passageways, the latter being particularly useful when fuel rich conditions are to be utilized.

The spacing of multiple precursor feeds is also, in general, geometrically repetitive, with spacings such as, for example, one precursor passageway for each 1 to 100 cm² of burner surface present. With suitable burners, the precursor passageway density may be higher or lower as desired.

The ability to tailor the conditions within a highly consistent high temperature zone allows production of a wide variety of nanoparticles. For example, tetramethyl tin, when used as a precursor, can be used to produce tin (0) nanoparticles, tin monoxide nanoparticles, and/or tin dioxide nanoparticles.

The ability to produce certain oxidation states of some elements may be limited by thermodynamic criteria. For example, it is difficult, perhaps impossible, to produce silicon metal nanoparticles by this method, whereas tin nanoparticles can easily be produced. Silicon oxides, particularly silicon dioxide, can be produced efficiently, however.

The surface of the MEDFB is preferably substantially planar. However, particularly with smaller devices, *i.e.*, those with 6 to 20 cm² of surface area, the flame temperature profile may decrease in temperature near the edges of the burner. In these areas, it may be desirable to raise the height of the passageways above the plane of those in the middle of the device to achieve a more one-directional temperature profile. Thus, in cross-section, the surface may be somewhat of a shallow elliptical, parabolic, hyperbolic, or other shape, with passageways in the middle of the device having a lower elevation than those near the edges.

The precursor may be mixed with either or both of the combustible gas and the combusting gas, preferably only with one of these, such that particle stoichiometry is rendered more uniform thereby. For zero valent or low valent oxidation states, mixing with the combustible gas is preferred, while for higher oxidation states, mixing with the combusting gas is preferred. Mixing may be accomplished by entraining precursor in a flowing gas stream, injecting precursor into the respective gas stream, etc. Precursor in the form of liquid may be distributed in the gas stream in the form of microdroplets by customary techniques, including but not limited to ultrasonic atomizers, sonolators, etc. Solid microparticles of precursor, dispersed in a gas stream, are also useful.

It is also possible to inject precursor into the flame through separate passageways through which no combustible or combusting gas flows. In this manner, the precursor supply rate may be decoupled from the supply rates for combusting and combustible gases. One such arrangement is to provide hollow tubes or "needles" within spaced passageways in the burner surface. The passageway in which the precursor supply needle is located may be isolated from other gases, or may be supplied with combusting or combustible gas. The precursor, when separately supplied in this manner, may be supplied in pure form, or admixed with combusting or combustible gas, may be admixed with a gas which is inert under the reaction conditions, *e.g.*, argon, helium, or in some cases, nitrogen, or may be mixed with a further non-reactive or reactive gas such as carbon monoxide, carbon dioxide, etc.

The spacing of precursor passageways may be adjusted, but it is desired that the passageways are arranged such that they may all be considered to be operating within the same chemical and thermal environment. The shape of the precursor plume is, in many cases, desired to be substantially radially symmetrical. However, sheet-like plumes may also be useful. In general, precursor inlets may be provided at densities of one inlet per 1 cm² to 500 cm² of burner surface area, more preferably 2 cm² to 100 cm², and most preferably 5 cm² to 50 cm².

Further description of the MEDFB may be had with reference to Figures 1 and 2. In Figure 1, an MEDFB 1 is illustrated in a cut-away view from the side, the number of passageways being limited for purposes of illustration. The alternating vertical bars 3 represent combustible gas passageways, while the alternating vertical bars 5 represent combusting gas passageways. The passages 3 are manifolded together with manifold 6, and supplied with combustible gas through gas supply 2. The combusting gas passageways 5 are similarly manifolded with manifold 8 and supplied with oxidizing (combusting) gas through gas supply 9. The top surface 10 of the burner is substantially planar.

Also shown in Figure 1 are surrounding passageway(s) 12 which is/are supplied by gas inlet 13 with a supply of gas, preferably inert, to form a "shroud" or envelope around the active portions of the flame above the burner. A mechanical shroud or "chimney" may also be employed, *i.e.* one of a refractory metal, ceramic, or glass, *i.e.* fused quartz. This chimney may be used with or without the gaseous shroud illustrated. For simplicity, the passageways 12 are shown on any one side of the burner, while they actually surround the entire perimeter.

Also shown in Figure 1 is a separate precursor supply passage 15, shown as a solid vertical bar, supplied with precursor or a mixture containing the precursor through precursor inlet 16. The combustible gas passageways may include within them an enclosed further passageway for supply of a combustible gas, and the separate precursor inlet used may also constitute a separate "tube within passageway" arrangement.

Figure 2 illustrates a magnified view of the top of a MEDFB looking down from above, having a honeycomb grid arrangement. The open hexagons 20 represent combustible gas or combusting gas passageways, while the hexagons 22 with an inscribed circle represent combusting gas or combustible gas passageways, respectively, *i.e.*, the gas supply to the open hexagons will be complementary to the supply of the inscribed circle hexagons. The hexagons 24 with shaded inscribed circles represent optional precursor inlets, which may be replaced by ordinary

combustible gas or combusting gas passageways when the precursor is entrained in one or more of the latter and not separately introduced.

The spacing of the precursor passageways 24 are preferably arranged in space such that a stable environment, particularly the environment surrounding the precursor "plume" (when used) is created. A typical burner may have 5 combusting gas hexagons which measure 0.5 to 2.0 mm, preferably about 0.8 mm between opposing flats of the hexagon, with a wall thickness of 0.02 to 0.1 mm, preferably about 0.5 mm. The combustible gas fuel tubes are preferably circular, preferably having a diameter between about 0.5 and 2.0 mm, and positioned to fit 10 within hexagonal passageways preferably identical in geometry to the combusting gas hexagons, *i.e.*, having an inner diameter of about 0.5 mm and outer diameter of about 0.8 mm. A device with a nominal surface area of about 6.5 cm², for example, may contain 173 combustible gas tubes, about 480 combusting gas passageways, and when used, a single precursor passageway located centrally. A 15 suitable burner for low volume production may be obtained as a Hencken burner, RD1x1, Research Technologies, and may be constructed of a high temperature resistant alloy such as Hastelloy. The latter burner has a 0.635 cm wide shroud surrounding the burner passageways.

In a commercially sized burner, it is anticipated that the surface area 20 of the burner may range from 100 cm² to 1 m² or larger. Alternatively, to conserve collection equipment, a plurality of smaller burners, of *i.e.* 10 cm² to 100 cm² may be operated in parallel, preferably surrounded in total by a chimney, or contained within a larger vessel with walls spaced from the burners.

The spacing and size of the passageways may be adjusted to obtain 25 the desired temperature and temperature profile, and passageways of 1 cm "diameter" are indeed feasible. However, smaller passageways are preferable to achieve a uniform one-dimensional temperature profile. Thus, the passageway diameters are preferably less than 5 mm wide, more preferably 0.5 to 2 mm wide.

The combustible gas and combusting gas are non-premixed. By “non-premixed” is meant that the individual gas streams are below the combustible limit under the conditions utilized. For simplicity, the combusting gas preferably contains no combustible gas and the combustible gas preferably contains no combusting gas. Precursors, also for simplicity, are preferably supplied either separately, or admixed with a gas stream in which they are either non-reactive or are present below the combustible limit. In more complex devices, it may be desired to add a minor portion of combustible gas with the combusting gas, and/or a minor portion of the combusting gas with the combustible gas. However, the amounts added will be such that the individual gas streams are still below the combustible limit. Combustible limits are available in tabular form, or may be determined experimentally. A gas stream which is incapable of “flash back” is also considered to be below the combustible limit for the purposes of the subject application.

The flame temperature may be adjusted by varying the pressure and hence rate of supply of the various gases, which will generally also affect gas velocity. While the flame temperature may also be adjusted by varying flame stoichiometry, this method of flame temperature may not be available in certain cases, *i.e.* where particle stoichiometry could be affected thereby.

An alternative method of varying flame temperature and thus flame profile, as well as residence time of the precursor and particles obtained therefrom in the flame, is to mix one or more of the combusting or combustible gases or precursor with a non-reactive gas. Such a non-reactive gas is preferably helium or argon, however in some syntheses, particularly at lower flame temperatures and stoichiometrically-rich conditions, nitrogen or other gases may be used. In oxygen rich stoichiometries, carbon dioxide may sometimes be used.

Varying the residence time in the flame will effect the particle size and particle size distribution. The particle formation may be envisioned, in many cases, as disclosed in M.S. Woolridge, “Gas Phase Combustion Synthesis of Particles,” PROG. ENERGY COMBUST. SCI., v. 20, pp. 63-87, 1998, page 64, where

initial reaction leads to “monomer” formation, which, in turn, lead successively to cluster formation followed by homogenous nucleation, agglomeration, agglomerate surface growth, and coalescence. In principle, short residence times favor homogenous nucleation and, limited agglomeration, without further increasing particle size, whereas long residence times favor greater agglomeration, agglomerate surface growth, and coalescence.

The combustible and combusting gas are not premixed, and no mixing takes place within the burner *per se*. Instead, rapid mixing takes place near the surface of the burner, producing an intense primary flame, which has the characteristics of a premixed flame above the mixing region, *e.g.* 3-5 mm from the burner surface. The flame produced is “one-dimensional,” *i.e.*, has temperature isotherms which are parallel with the burner surface. Transverse temperature profiles obtainable with a 2.54 x 2.54 cm laboratory scale burner are shown in Figure 3. Note that at heights from about 5 mm to 20 mm, the temperature decreases only from 1600°K to 1400°K, and that at each height, the temperature is relatively constant in the transverse direction. These temperatures were measured using H₂/O₂/Ar with an H₂ velocity of 1.44 m/s and an O₂/Ar velocity of 1.15 m/s, at 2:1 stoichiometry (H₂:O₂), on a mole/mole basis. Argon was premixed with oxygen, and the Ar flow rate was 18.0 L/min.

Figure 4 illustrates temperature in the axial direction (orthogonal to the burner surface), at a slightly lower Ar flow rate of 17.8 L/min. It can be seen that from about 10 mm to beyond 30 mm, the temperature is virtually constant. The ability to adjust temperature by means of flame stoichiometry is demonstrated by Figure 5. It should be noted that stoichiometry changes also influence the oxidizing/reducing character of the flame.

Introduction of precursor into the combustible or combusting gas streams exposes the precursor to the high temperature environment of the primary flame, *e.g.* 1600°K to 1800°K (Figure 4). The precursor and/or particles, monomers, etc., then experience a relatively constant and somewhat lower temperature as they travel away from the burner surface. The relatively constant

temperature produces steady state conditions which favor relatively uniform particle sizes and morphology.

5 If instead of being premixed with the combustible or combusting gas, the precursor is fed to the flame separately, a diffusion flame is created where oxidizing and/or reducing species are derived from the primary flame. By altering the primary flame stoichiometry, and optionally the combusting gas or combustible gas content of the precursor feed, an oxidizing, moderately oxidizing, or reducing chemical environment may be created.

10 The process of the present invention exhibits unusual combustion behavior which results in the ability to provide a variety of particles by changes in the flame stoichiometry, flow rates, inert gas dilution, etc. Most surprising is the ability to generate particles of zero valent metals in some cases, and particles of one or more higher oxidation states of the same metal employing different conditions. The stability and uniformity of the flame front and high temperature zone also
15 allows for the production of highly uniform and very small particles at reasonable production rates, not possible with other systems.

Product collection may be performed by conventional techniques, including chill plates, bag filters, etc. If coatings of the nanoparticles are desired, the substrate to be coated may be positioned at an appropriate distance, and particles
20 allowed to impinge upon its surface.

Examples

The subject invention is illustrated by the following examples, which are performed on a laboratory scale MEDFB. The MEDFB consists of a planar honeycomb array having outside dimensions of 2.54 x 2.54 cm, surrounded by a
25 shroud gas passageway 0.635 cm wide. The honeycomb passageways measure 0.813 mm with wall thicknesses of 0.051 mm. Circular cross-section fuel tubes are spaced within the honeycombs in the array, each fuel tube surrounded by six oxidizer channels. A single precursor inlet is centrally located in the array. There

are approximately 173 fuel passageways and 480 oxidizer passageways. The shroud channels are composed of hexagonal passageways identical to those of the burner surface. The arrangement of the burner surface corresponds generally to that of Figure 2, but with only one separate precursor inlet passageway.

5 The MEDFB is mounted on a two-axis translation stage, allowing the burner to be moved horizontally and vertically, facilitating optical and physical sampling of the product gases and particles. By translating the burner, SiO₂ particles may be sampled as a function of distance above the surface of the burner (*i.e.* as a function of residence time) directly onto transmission electron microscope (TEM)
10 grids (3.05 mm diameter, carbon film on copper 300 mesh grids, Electron Microscopy Science, CF300-C450). The TEM samples are obtained by fixing the grids onto the end of a stainless steel sampling probe, which is connected to an air-driven pneumatic piston/cylinder device (100 mm stroke). The piston rapidly inserts the sampling probe into the flame or product region allowing the particles to deposit
15 onto the grid via thermophoresis. Thermophoretic sampling is a well-established method for obtaining particles representative of the sampling location in combustion systems. All sampling times are less than 0.27 s (as measured using a timing circuit activated by the valve triggering signals). The majority of the sampling time is attributable to the probe transit time (*i.e.* the time to traverse through the ambient
20 surroundings and to the target x-y location above the burner). Because the combustion system is one-dimensional and the probe travels though an x-y plane parallel to the surface of the burner, all particles deposited onto the TEM grid experience the same combustion conditions and are representative of the particular sampling height. In particular, the probe is aligned such that the grids are inserted
25 parallel to the flow, and samples are taken as the probe travels in an x-y plane to an $x = 0$ mm, $y = 0$ mm, or an $x = 0$ mm, $y = 5$ mm location. Samples obtained at the off-center location indicates that variations in the flow field (introduced by the absence of fuel in the optional precursor inlet tube) does not affect the sampling results. The particle size, size distribution and morphology of the SiO₂ powders
30 may be examined using transmission electron microscopy (JEOL 4000EX) to image the particles. Images may be taken at high (x40k) and moderate (x10k)

magnifications to ensure resolution of both the small primary particles and the larger aggregates.

Bulk samples of the powders may be also collected for *ex situ* analysis using a cold plate located in the exhaust region above the burner (~23 cm above the surface of the burner). Nitrogen adsorption (BET, Micromeritics ASAP 2010 Accelerated Surface Area and Porosimetry System) is used to determine the specific surface area of the product powders.

Temperature profiles above the surface of the burner are obtained using water absorption spectroscopy and fine wire platinum-platinum/10% rhodium thermocouple measurements (0.05 mm diameter, type S thermocouple, Omega P10R-001). All thermocouple measurements are corrected for radiation effects and have an estimated uncertainty of $\pm 10\%$, which is primarily due to uncertainties in the physical properties of the thermocouple and the flow (*e.g.* bead shape, temperature dependent emissivity, etc.). All temperature measurements are made off-center of the burner to avoid non-uniformities caused by the central fuel tube. Point measurements are made in non-particle forming flames using the fine-wire thermocouples. Line-of-sight averaged temperatures may be obtained in both particle forming and non-particle forming flames using differential absorption spectroscopy of the water vapor naturally present in the product gases. Details of the diagnostic approach are provided in Torek, P.V., Hall, D.L., Miller, T.A., and Wooldridge, M.S., "H₂O Absorption Spectroscopy for Determination of Temperature and H₂O Concentration in High-Temperature Particle Synthesis Systems," *Appl. Optics*, . 41 pp. 2274-2284; and Torek, P.V., Hall, D.L., Miller, T.A., and Wooldridge, M.S., in "Characterization of a Multi-Element Diffusion Burner for Combustion Synthesis Studies, in Fundamental Gas-Phase and Surface Chemistry of Vapor Phase Deposition II", Swihart, Allendorf, Meyyappan and Seal Eds., The Electrochemical Society, Inc., ECS Proceedings, Vol. 2001-13, pp 213-220. Briefly, near infrared emission from a tunable semiconductor diode laser is rapidly modulated across several absorption line shapes of H₂O spectra at ~1.39 μm . The path-averaged temperature is determined using the relative peak heights of the absorption lines. The laser emission is multi-passed and aligned orthogonal to the

direction of the flow. Cold water vapor present in the room air and product water vapor entrained in the shroud region are accounted for in the data analysis. Therefore, the results using the H₂O absorption diagnostic represent average temperatures in the x-y plane in the high-temperature, core region of the burner.

5 The MEDFB can be operated over a broad range of flow rates using a variety of particle precursor reactants to produce steady, laminar flame conditions. In this study, silane (99.99% SiH₄, Cryogenic Gases) is used as the precursor reactant to form silica particles. Small amounts of silane (premixed in argon: 18.5% SiH₄, balance Ar; mole basis) are mixed with hydrogen (99.99% H₂, Cryogenic
10 Gases) and introduced into the fuel tube array of the burner. Premixed oxygen (99.995% O₂, Cryogenic Gases) and argon (99.998% Ar, Cryogenic Gases; 7.4% O₂ premixed in Ar, mole basis) flow through the oxidizer channels, while nitrogen (99.998% N₂, Cryogenic Gases) is used as the shroud gas. All flow rates are controlled using calibrated rotameters (Omega, $\pm 5\%$ accuracy). The reactant gases
15 exit the tubes and channels and mix rapidly above the surface of the burner. As a result, an array of small SiH₄/H₂/O₂/Ar diffusion flames or a dimpled flame sheet is formed. Silica (SiO₂) nanoparticles are created as products of the diffusion flames.

 Burner performance is characterized using both particle forming (SiH₄/H₂/O₂/Ar) and nonparticle forming (H₂/O₂/Ar) flames. All experiments are
20 conducted at atmospheric pressure. The reactant flow rates are summarized in Table 1. Equivalence ratios (ϕ), also listed in Table 1, are the quotients of the actual fuel-to-oxygen ratios divided by the stoichiometric fuel-to-oxygen ratio. Stoichiometric conditions are assumed to lead to complete conversion of all silicon to SiO₂ and all hydrogen to H₂O. The experimental procedure consists of keeping the O₂ and Ar
25 flow rates constant and changing the fuel-to-oxidizer ratios by increasing the H₂ flow rates. The silane (premixed 18.5% SiH₄, balance argon; mole basis) is then fed in approximately fixed proportion to the hydrogen flow rate for each equivalence ratio condition. Therefore, increasing the equivalence ratio also corresponds to increasing silane loading.

The velocity of the reactants can be estimated based on the measured total volumetric flow rates and the known dimensions of the fuel tubes and oxidizer channels. For typical operating conditions (*e.g.* $\phi = 1$, $\text{H}_2/\text{O}_2/\text{Ar}$ flame), the velocity of the fuel gases exiting the tubes is $V_{\text{fuel}} \approx 1.44$ m/s and the velocity of the oxidizer gases is $V_{\text{O}_2/\text{Ar}} \approx 1.15$ m/s. The corresponding Reynolds numbers for the unreacted gases are $\text{Re}_{\text{D,fuel}} = 6.6$ and $\text{Re}_{\text{D,O}_2/\text{Ar}} = 67$. Hence, small laminar diffusion flames are formed above the fuel tubes, resulting in an array of approximately 173 diffusion flamelets.

No visible emission is evident from the $\text{H}_2/\text{O}_2/\text{Ar}$ flames or when small concentrations of silane are added to the reactants. At higher silane concentrations, orange emission (from silica particles entrained in the product gases) becomes apparent (see Fig. 3). Although particle accumulation on the surface of the burner can occur at a high rate at very high-particle loading conditions, all the experimental data presented is obtained at conditions where particle accumulation is insignificant, (*i.e.* where the highest silane loadings leads to significantly less than 1 mm of material present at any location and before any fuel tubes might become obstructed). In addition, the burner is carefully cleaned of all material before each operation. Note that some obstruction to the fuel tubes is generally visible for most operating conditions during combustion synthesis studies.

Measurements of the temperature profiles above the surface of the burner are made using absorption spectroscopy for both particle forming and non-particle forming flames and using thermocouples for non-particle forming flames. Rapid mixing of the combustion gases ideally leads to a top-hat temperature profile in the x-y plane above the surface of the burner. Both the spectroscopic and the thermocouple measurements indicate steep temperature gradients very near the surface of the burner (below approximately 5-7 mm), where the diffusion flamelets are formed. Above this region, the temperature profiles in the vertical and horizontal directions are quite uniform. For example, Figure 3 shows thermocouple data in the x-y plane parallel to the surface of the burner for typical non-particle forming flame conditions. The effects of fuel/oxidizer mixing are observed in the $z = 5$ mm data. However, there is typically less than $\pm 3\%$ variation in temperature

from the mean value in the core region (*i.e.* $x < \pm 11$ mm) for heights above $z = 10$ mm. Figure 4 shows the results of thermocouple measurements as a function of height above the burner for an equivalence ratio of $\phi = 1.0$. The six lines shown in the figure represent three vertical traverses of the thermocouple in the upward
 5 direction and three complementary traverses in the downward direction, taken on three separate occasions. The thermocouple data shown in Figs. 3 and 4 indicate that approximately constant temperatures extend from $z = 10$ mm to greater than $z = 40$ mm above the surface of the burner. The temperature measurements also indicate the core high-temperature region shrinks slightly with vertical distance, *e.g.*
 10 core region $x \leq \pm 10$ mm at $z = 30$ mm. Figure 5 shows thermocouple results for three equivalence ratio conditions, demonstrating the same quality of performance can be achieved over a range of burner operating conditions. In addition, the axial uniformity of the MEDFB has been confirmed via OH absorption spectroscopy of $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ flames. In Figure 5, the “diamond” data are for $\phi = 1.2$, the
 15 “triangles” for $\phi = 1.0$, and the blackened circles for $\phi = 0.8$, all at a position of $x = -0.5\text{mm}$, $y = + 6.75$ mm.

For hydrogen flames doped with low levels of silane, typical of the examples, the adiabatic flame temperature is approximately equal to that of an undoped hydrogen flame of the same fuel to oxygen ratio and argon dilution level.
 20 For example, for $\phi = 1.0$, for a doped flame with $\text{SiH}_4 = 0.049$ 1pm, $\text{H}_2 = 2.47$ 1pm, $\text{O}_2 = 1.32$ 1pm, $\text{Ar} = 16.7$ 1pm, $T_{\text{ad}} = 1745$ K; whereas for an undoped flame with $\text{H}_2 = 2.67$ 1pm, $\text{O}_2 = 1.32$ 1pm, $\text{Ar} = 16.7$ 1pm, $T_{\text{ad}} = 1696$ K. Therefore, thermocouple measurements in non-particle producing flames are representative of temperatures of particle producing flames of the same fuel to
 25 oxygen ratio and argon dilution level. The temperatures measured using the H_2O absorption spectroscopy are all lower than the equilibrium determinations. However, the thermocouple measurements and the OH absorption spectroscopy measurements of temperature confirm adiabatic behavior at fuel rich conditions. The systematically lower temperatures obtained using H_2O absorption spectroscopy
 30 are likely due to uncertainties in the collisional broadening data used in the spectroscopic model. The improved agreement with adiabatic equilibrium calculations at fuel rich conditions is attributed to lower heat losses to the burner at

$\phi > 1.0$ due to the higher reactant flow rates. At lower equivalence ratios and therefore lower reactant flow rates, the flame sheet will be located closer to the burner surface and will experience greater heat loss.

As mentioned above, the ability to predict the product composition and temperatures using adiabatic equilibrium calculations represents another advantage of the MEDFB system. The power of equilibrium calculations for planning and conducting combustion synthesis research has been well documented in the combustion literature including the seminal work by Glassman et al., "A Gas-Phase Combustion Synthesis for Non-Oxide Ceramics", 24th Symp (Int.), COMBUSTION, pp. 1877-1882, and the comprehensive review by K. Brezinsky, "Gas-Phase Combustion Synthesis of Materials," 26th Symposium (Int.), COMBUSTION, pp. 1805-1816. MEDFB experiments can be readily designed to explore reactant-to-product conversion efficiencies, product compositions, and material phase diagrams.

Silica powders are sampled and imaged to determine the microstructural particle properties and statistics as a function of height above the surface of the burner. Both agglomerates and discrete (i.e. individual or primary) particles, spherical in shape, are apparent in particles sampled at $\phi = 1.01$ conditions at a height of $z = 10$ mm. The diameters of the primary particles were determined by direct measurement from the TEM images. Particle size bins were stipulated to facilitate acquiring the particle statistics, and the same particle size bins are used for all image analyses. Particles below 5 nm in diameter are either not present or below the resolution of the TEM imaging for all conditions studied.

The primary particle size distribution (normalized by the width of the size bins) as a function of distance above the burner is shown in Fig. 6 for $\phi = 1.01$. The horizontal error bars shown for the $z = 10$ mm data denote the extent of the particle size bins. Relatively coarse size bins were used. It was found that a log-normal population function $P(d_p)$ may be used to represent the particle size distributions for the low silane loadings or low equivalence ratios with relatively good agreement with the experimental data. The geometric mean diameter of the

primary particles, \bar{d}_p , for each height is also determined, and the results are presented in Fig. 7. The error bars in Fig. 7 represent the uncertainty in the measurements (~15%) due to the combined effects of the particle bin sizes and the total number of particles counted.

5 The geometric standard deviation of the geometric mean particle diameter σ_g , may also be determined from the TEM images. The results for σ_g were between 1.48 and 1.66 for all conditions and heights examined; however, because sample sizes of less than 1000 particles are used to obtain the σ_g data, the results may have high uncertainties. Note that the values for σ_g are very near the self-
10 preserving particle size limit for coagulation of $\sigma_g = 1.45$ determined by Pratsinis and co-workers, indicating a self-preserving limit has been reached in the MEDFB system for the conditions studied.

 The particle microstructure observed is consistent with the literature on the relative sintering and coagulation rates for SiO_2 . The low-pressure limit for
15 silane decomposition ($\text{SiH}_4 + \text{M} \rightarrow \text{SiH}_2 + \text{H}_2 + \text{M}$),

$$k \text{ (cm}^3\text{/s/mol)} = 3.68 \times 10^{30} T^{3.95} \exp(-58,040 \text{ (cal/mol)/RT}) \quad (1)$$

may be used to estimate the characteristic time for chemical reaction. The coagulation time may be estimated assuming a monodisperse aerosol of spherical silica particles ($\bar{d}_p = 11 \text{ nm}$, $\rho_{\text{SiO}_2, \text{amorphous}} = 2.196 \text{ g/cm}^3$) and using the collision
20 frequency for the free molecular regime. The characteristic time for sintering is determined using the relation developed by Xiong et al. for sintering of ultrafine silica:

$$\tau_{\text{sinter}} = 5.5 \times 10^5 \bar{d}_p \exp\left(\frac{1565(K)}{T}\right) \quad (2)$$

where \bar{d}_p has units of cm. An approximate particle residence time for silica
25 particles sampled from the MEDFB system at $z = 75 \text{ mm}$ is also identified in Fig. 8. The particle residence time was estimated for an ideal case where a particle is produced in the core region of the MEDFB where the temperature and velocity

profiles are uniform and constant and the particle is sampled at a known height above the burner. Using the gas velocity at the exit plane of the burner ($V \approx 1$ m/s), assuming acceleration of the gases by a factor of ~ 3 , a particle residence of 25 ms is determined.

5 As seen in Fig. 8, coagulation dominates compared to sintering throughout the range of conditions studied. This is consistent with TEM images of the particles sampled from the MEDFB system, where both agglomerates and discrete spherical particles are present at all sampling conditions and locations. If the sintering rates were very rapid compared to the coagulation rates, only spherical
10 particles would be observed.

Bulk silica samples are analyzed using BET for two representative equivalence ratios. The resulting specific surface areas are 218 m²/g for $\phi = 0.84$ and 187 m²/g for $\phi = 1.80$. Assuming spherical particles and using the density of amorphous silica, the specific surface areas can be converted to average particle
15 diameters via

$$\bar{d}_{p,SSA} = \frac{6}{SSA \rho_{SiO_2}} \quad (4)$$

where $\rho_{SiO_2, amorphous} = 2.196$ g/cm³, resulting in $\bar{d}_{p,SSA} = 12.5$ nm for $\phi = 0.84$ and $\bar{d}_{p,SSA} = 14.6$ nm for $\phi = 1.80$. Because the bulk samples are obtained in the exhaust region, the characterization results indicate properties of long residence time
20 particles. The results for determined via the BET measurements are consistent with the TEM analysis. However, the average particle diameters are higher than those determined from the TEM images, which is typical of powders where necking and bridging occur between primary particles. The BET data support the conclusion that coagulation dominates the particle growth mechanisms and sintering between
25 primary particles is not complete at the MEDFB conditions studied. Production of particles without sintering and/or with minimal necking is desirable for many applications.

The MEDFB performance and particle statistics can be compared to results of canonical studies of other benchmark burner configurations using the same reactants for silica synthesis, such as the counterflow diffusion flame systems examined by Chung and Katz and Zachariah et al. and the low pressure premixed flat-flame burner system examined by Lindackers et al. The transverse temperature profiles observed in the MEDFB studies are of comparable quality to that which can be obtained in counterflow diffusion burner systems. For example, Chung and Katz have demonstrated transverse temperature profiles with variations of less than ~ 25 K (or less than $\sim 2\%$ variation from the mean value) in the core region of their counterflow diffusion burner using $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ reactants, compared to the $< 3\%$ variations found in the core region of the MEDFB. A key difference between the MEDFB and counterflow burner systems is the ability to produce sustained regions of approximately constant temperatures along the particle streamlines, i.e. as a function of the axial coordinate z . The axial uniformity of the MEDFB temperature profiles is also excellent, with less than $\pm 2.5\%$ variation in the mean temperature in the region from $z = 10$ mm to $z = 30$ mm for equivalence ratios $\phi = 0.8 - 1.2$. Thus the axial thermal uniformity of the MEDFB is of comparable or better quality than that observed in combustion synthesis studies using premixed flat-flame burners. This characteristic of the MEDFB has considerable promise for studies of fine particle sintering rates at high temperatures, where interpretation of particle morphology data is greatly simplified by the constant temperature profiles.

In general, the qualitative trends in the particle statistics of the current work are consistent with previous studies using silane as a silica particle precursor. Zachariah and coworkers found $\bar{d}_{p,SSA} \approx 30 - 150$ nm based on laser scattering measurements in their studies of $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ counterflow diffusion flames. Comparable silane loadings were used in the MEDFB study as were used in the counterflow burner study. However, Zachariah et al. observed much lower particle number densities ($10^4 - 10^8$ particles/cm³) than with the MEDFB studies. Assuming complete conversion of the silane to silica particles and using a representative particle diameter of $d_p \approx 12$ nm, results in silica particle loadings of $\sim 6.8 \times 10^{11}$ particles/cm³ in the MEDFB system. Therefore agglomeration effects will be different in an MEDFB compared to a counterflow condition. Agglomerates in a

counterflow system will have relatively more time between collisions to coalesce and grow to larger sintered spherical shapes, particularly given the higher temperatures of the counterflow burner system (peak temperatures from $T = 1986\text{--}2535\text{ K}$).

- Lindackers and coworkers examined silica synthesis using premixed $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ flat flames. Very low pressures were used to extend the reaction zone and to suppress particle formation within the body of the burner. Although the silane loadings, pressures, equivalence ratios and dilution levels used in their study ($\text{SiH} < 600\text{ ppm}$; $\text{Ar}/(\text{H}_2 \pm \text{O}_2) = 1.04, 1.36$; and $P \approx 0.03\text{ atm}$) were significantly different from those used here, the premixed flat-flame results for \bar{d}_p are consistent with expectations. It should be noted, however, that the silica density used to calculate the particle diameters was 2.65 g/cm^3 , or 20% larger than the value used here.) The lower pressures result in particles that are smaller than those observed in the pseudo flat-flame environment of the MEDFB for a similar z -location.

Table 1. Experimental conditions of SiO₂ synthesis

	ϕ^*	SiH ₄ [lpm]	H ₂ [lpm]	O ₂ [lpm]	Ar [lpm]	N ₂ shroud [lpm]
5	0.42	0.000	1.12	1.32	16.4	28.3
	0.47	0.029	1.13	1.32	16.6	28.3
	0.69	0.000	1.81	1.32	16/4	28.3
	0.75	0.039	1.82	1.32	16/6	28.3
	0.84 ^a	0.049	2.47	1.58	16.7	28.3
10	0.93	0.000	2.45	1.32	16.4	28.3
	1.01	0.049	2.47	1.32	16.7	28.3
	1.39	0.000	3.68	1.32	16.4	28.3
	1.51	0.068	3.71	1.32	16.7	28.3
	1.80 ^a	0.097	5.31	1.58	16.9	28.3
15	2.00	0.000	5.29	1.32	16.4	28.3
	2.16	0.097	5.31	1.32	16.9	28.3
	0.80 ^b	0.000	2.35	1.47	18.5	28.3
	0.80 ^b	0.000	2.35	1.47	17.8	28.3
	1.00 ^b	0.000	2.93	1.47	18.5	28.3
20	1.00 ^b	0.000	2.93	1.47	18.0	28.3
	1.00 ^b	0.000	2.93	1.47	17.8	28.3
	1.20 ^b	0.000	3.53	1.47	17.8	28.3
	1.50 ^b	0.000	4.41	1.47	18.5	28.3

*For the equivalence ratio determinations, both hydrogen and silane are considered in the fuel concentrations.

^aOperating conditions used to obtain the bulk samples analyzed using N₂-adsorption BET.

^bConditions used to obtain thermocouple data.

25

Results

Examples are also performed using a tin precursor. Silicon and tin are useful representations of metals useful in the process of the subject invention due to the relative stability of the +4 oxidation state of silica at high temperatures, whereas tin oxidation states are both somewhat stable. Thus, silicon typifies metals

which generally produce only particles of one oxidation state, i.e. SiO_2 , whereas tin is representative of metals whose oxidation state can be adjusted by varying flame temperature and stoichiometry.

5 The procedures used for study of particles produced from tin precursors, tetramethyl tin here, are substantially the same as with silane. However, in these examples, the precursor was added via the precursor inlet passageway as opposed to being fed to the primary flame.

10 Table 2 is a summary of the experimental conditions and the results which may be obtained for powder composition and material production rates. The effects of three important synthesis parameters are considered: (1) the local level of oxygen-containing species available for reaction with $\text{Sn}(\text{CH}_3)_4$, (2) the temperature of the primary flame, and (3) the particle residence time at high temperatures. The oxygen species concentrations are controlled by changing the equivalence ratio (ϕ , the quotient of the actual fuel-to-oxygen ratio of the reactants
15 divided by the stoichiometric fuel-to-oxygen ratio) of the primary flame. The TMT of the secondary flame is not considered in the determination of the equivalence ratio of the primary flame. The temperature of the primary flame is examined by changing the dilution level of the primary flame reactants with argon, while maintaining a constant equivalence ratio. Particle residence time effects are
20 examined by sampling materials at various distances from the burner surface, extending the regions of high temperatures via use of a chimney and by changing the volumetric flow rate of the TMT/Ar gases.

Powder composition is determined by comparison of the XRD patterns of the powder samples with accepted standards for SnO_2 , SnO and Sn .
25 SnO_2 peaks all indexed to the tetragonal crystallographic phase of $\alpha\text{-SnO}_2$ or the cassiterite form of tin dioxide. SnO peaks indexed to the romarchite form of tin monoxide, and Sn peaks indexed to metallic tin. All XRD analyses of white powder samples index to SnO_2 , yellow/brown powder samples index to SnO , and gray powder samples index to Sn . Therefore, the sample color is considered a good
30 indication of the material composition.

As indicated by the results shown in Table 2, the most important parameters in determining the composition of the product powders are the equivalence ratio and temperature of the primary flame. For near stoichiometric or fuel lean operation ($\phi \leq 1.0$) at moderate temperatures, SnO_2 is formed. For fuel rich conditions ($\phi > 1.0$), both SnO and Sn are formed. The composition of the bulk materials varies as a function of location on the sample coupon. Due to the geometry of the secondary flame (i.e. radial symmetry), the powder depositions are nonuniform in composition for the fuel rich conditions, with lower levels of tin oxidation found near the center of the samples. Because it is difficult to isolate the Sn from the SnO samples and vice versa due to the lack of a distinct transition from Sn to SnO on the sample coupons, some Sn and SnO XRD patterns indicate small peaks attributable to the alternative material. No compositional variation is observed with the $\phi \leq 1.0$ samples obtained at moderate temperatures, and no Sn or SnO peaks are identified in the SnO_2 XRD patterns.

Changing the equivalence ratio changes the temperature of the primary flame. However, in order to isolate temperature from equivalence ratio effects, experiments are performed where ϕ is kept constant and argon dilution of the primary flame was altered. Reducing the argon dilution of the primary flame increases the temperature of the primary flame. Increasing the temperature of the primary flame leads to added decomposition of the products of the primary flame and essentially “preheats” the species from the primary flame that participate in the secondary flame system. A 37% change in the argon flow rate to the primary flame leads to a 27% change in the predicted adiabatic flame temperature in the burner used. Decreasing the argon flow rate to the primary flame is not expected to have a significant effect on the residence time of the particles formed in the secondary flame, due to the large difference in velocities of the gases in the primary and secondary flames. For example, the exit velocities of the TMT/Ar reactants from the secondary flame vary from approximately 8.6-97 m/s ($Q_{\text{TMT}/\text{Ar}} = 35\text{-}395$ mlpm), with the majority of the experiments at 15-20 m/s conditions. The exit velocities of the $\text{H}_2/\text{O}_2/\text{Ar}$ reactants from the primary flame are approximately 1-2 m/s ($Q_{\text{H}_2} = 2.9$ lpm, $Q_{\text{O}_2} = 1.5$ lpm, $Q_{\text{Ar}} = 18.5$ lpm) for most experiments. However, decreasing the argon flow rate of the primary flame would serve to increase the

particle residence time at high temperatures, thereby intensifying the effects of increasing the primary flame.

5 The maximum temperature of the primary flame, T_{ad} , can be estimated using adiabatic equilibrium calculations and the known equivalence ratio and level of argon dilution of the primary flame. The calculated values for T_{ad} are provided in Table 2 as an indication of the magnitude of the changes in the primary flame temperatures examined.

10 In addition to the equivalence ratio, the temperature of the primary flame is found to be a significant factor affecting the material composition. Higher temperatures (lower argon concentrations) leads to formation of Sn and SnO at $\phi = 0.99$, a condition where previously at lower primary flame temperatures only SnO_2 was produced. The change in the powder composition as the temperature of the primary flame is increased is consistent with model predictions.

15 Changing the TMT/Ar flow rate, varying the sampling location and/or using the chimney to affect particle residence times, for all cases where $\phi \leq 1.0$ and the dilution of the primary flame is moderate, i.e. primary flame temperatures are moderate, has no effect on the material composition. SnO_2 is produced in all cases (see Table 2). For conditions where $\phi > 1.0$ or conditions with low dilution of the primary flame reactants, i.e. primary flame temperatures are high, if the Sn and SnO samples are not obtained before significant mixing with room air occurred, the tin would further oxidize to form SnO_2 . For example, comparing Examples 15 and 16 listed in Table 2, which have approximately the same equivalence ratio, $\phi \approx 1.2$ -1.3, and TMT/Ar flow rate, both without the use of a chimney), sampling 9 cm higher in the exhaust region provides the particles with sufficient time at high temperatures to lead to complete oxidation of the tin. Collectively, the study of particle residence time effects indicate that oxidation of tin species occurs rapidly provided sufficient oxygen is available locally for reaction.

The effects of burner operating conditions on particle size and morphology characteristics are also investigated. For all conditions examined, the powders consist of both discrete nanosized primary particles and particle aggregates. The crystalline nature of the particles as shown by photomicrographs is clearly
 5 evident, and different lattice fringe orientations indicated sintering is relatively slow between particles.

Particle size distributions are obtained for selected TEM samples. Results for a typical fractional population for synthesis of SnO₂ nanoparticles are shown in Fig. 9. Note the low nanosize particle sizes. The particle size statistics
 10 are obtained using the methods previously described. However, a larger number of particles are counted (N > 800), in order to ensure more accurate particle statistics: geometric mean particle diameters, \bar{d}_p , change by less than 3% with the incorporation of additional particle count data. In general, the geometric mean particle diameters of primary particles sampled from the secondary flame are less
 15 than 12 nm, and particle aggregates are less than 100 nm in size (maximum chord length). The particle size distributions are relatively well represented by log-normal population distributions (see Fig. 9), and there is little variation in the particle size statistics as a function of height above the burner for the sample locations examined via TEM imaging.

20 Specific surface area (SSA) measurements of bulk samples obtained in the exhaust region of the burner are used to estimate the average particle size of the final product materials. Values for SSA for $\phi = 0.75$, $\phi = 1.00$ (TMT/Ar = 80.7 mlpm), and $\phi = 1.19$ are 37.6 m²/g, 36.2 m²/g, and 15.0 m²/g, respectively. Although the particles are not spherical, to a first approximation, the average
 25 particle diameter via SSA can be determined using

$$\bar{d}_{p,SSA} = \frac{6}{SSA \rho_{(SnO_2 \text{ or } Sn)}}$$

Based on the compositional analysis described above, for $\phi \leq 1.0$ with moderate primary flame temperatures, the density for SnO₂ (6.85 g/cm³) is used. For high

temperature conditions and/or $\phi > 1.0$, the density for Sn (5.77 g/cm^3) is used. For the SSA values provided above, the values for $\bar{d}_{p,SSA}$ are 23.3 nm ($\phi = 0.75$), 24.2 nm ($\phi = 1.00$) and 69.4 nm ($\phi = 1.19$). The larger dimension for the Sn particles compared to the SnO_2 particles is consistent with the lower melting point of Sn compared to SnO_2 ($T_{mp,Sn} = 231.9 \text{ }^\circ\text{C}$, $T_{mp,SnO_2} = 1630 \text{ }^\circ\text{C}$). The Sn particles will sinter more rapidly both in the secondary flame and on the collection plate, leading to coarser particles.

The particle sizes determined using BET are larger than those determined using TEM imaging; which is consistent with the respective sampling conditions. The BET and TEM particle sizes are obtained at dramatically different particle sampling times and sampling locations. The BET samples, yielding larger particle sizes of $\bar{d}_{p,SSA} = 23\text{-}24 \text{ nm}$ for SnO_2 , are obtained from the exhaust region of the burner (i.e. longer residence times) using comparatively long sampling times (minutes). The TEM samples, yielding smaller particle sizes of $\bar{d}_{p,TEM} = 10\text{-}12 \text{ nm}$ for SnO_2 , are obtained directly from the secondary flame using very short sampling times ($< 1 \text{ sec}$).

Although particle sizes determined by SSA are inherently larger than those determined by TEM imaging when necking and bridging occurs between primary particles, a comparison of the TEM and BET results for SnO_2 indicates that either significant particle growth is occurring in the secondary diffusion flame or significant particle restructuring is occurring on the sampling coupon on the cold plate. Therefore, the BET results for particle size represent an upper limit to the dimensions of the particles produced using this technique.

Mass production rates are measured for several samples to provide an indication of the potential manufacturing rates achievable (see Table 2). The corresponding maximum predicted production rates based on the known TMT/Ar flow rates and saturation levels (assuming 100% conversion efficiency) are also determined and reported. All the experimental values are significantly below the predicted values. However, the differences are not likely due to low reactant-to-product conversion efficiencies, as much as due to the low collection efficiency of

the bulk sampling method used. Material can bypass the cold plate and/or deposit on the cold plate outside the sample coupon region. Although the particle production rates are low compared to commercial powder production methods employing large, conventional burners, the MEDFB synthesis technique is not optimized for maximum production rates. In addition, the synthesis approach can be scaled to increase production rates by increasing the x-y dimension of the burner and incorporating additional secondary fuel tubes into the honeycomb matrix of the primary flame. Although the optimal spacing of the additional secondary fuel tubes can be adjusted, preliminary results indicate a spacing of 1.25 cm between secondary fuel tubes is sufficient for burners with multiple precursor supply passageways.

The results for composition and particle morphology may be interpreted using chemical kinetic and equilibrium models of the synthesis environment. Good agreement between one-dimensional premixed modeling of the primary flame and measured radical profiles can be obtained by incorporating detailed chemical kinetics in the model simulations. While a one-dimensional premixed model does not accurately describe the mixing conditions in the first few millimeters above the burner surface, the results can be used to infer trends above (i.e. downstream of) the initial mixing region. Figure 10 shows the model results for the minor and major species of the primary flame for a typical stoichiometric condition. The temperature profile used in the model is a polynomial fit to a measured temperature profile of the primary flame system when the secondary fuel tube is not used for particle synthesis. The chemical kinetics model does not include the effects of the secondary flame, including any chemistry associated with the TMT. As seen in Fig. 10, O_2 is rapidly consumed within 0.5 cm of the surface of the burner by the H_2 in the primary flame. At typical operating conditions, including $\phi = 1.0$, there is insufficient O_2 in the immediate vicinity of the secondary fuel tube (i.e. the surrounding 6 oxidizer channels) to completely oxidize the $Sn(CH_3)_4$ to complete products of combustion, i.e. SnO_2 , CO_2 and H_2O . For reference, a schematic of the secondary flame is superimposed on the results in Fig. 10. It is clear that although some of the TMT is oxidized by reaction with O_2 , a potentially significant portion of the TMT and/or Sn and SnO particles (produced

by the locally rich secondary flame) are likely oxidized by reaction with H_2O , the most abundant oxygen-containing species present in the co-annular region surrounding the secondary flame. Given the high purity of the SnO_2 product observed for the moderate temperature $\phi \leq 1.0$ conditions, and the rapid oxidation of Sn and SnO particles by room air for $\phi > 1$ conditions, it may be concluded that the chemical kinetics of the TMT/ SnO_x particle system is rapid compared to the molecular mixing of the reactants. In addition, if diffusion of oxygen into the center of the Sn or SnO particles was slow, a core/mantle type structure would be observed in the TEM images and mixed $\text{SnO}_2/\text{SnO}/\text{Sn}$ XRD compositions, rather than the TEM images and high purity SnO_2 XRD profiles that are obtained.

Equilibrium calculations which include tetramethyl tin and tin species provide additional insight into the chemistry of the TMT/ $\text{H}_2/\text{O}_2/\text{Ar}$ system and aid in interpretation of the observed temperature and equivalence ratio dependence to the SnO_x compositions. Figures 11 and 12 present the moles of product tin species as a function of the equivalence ratio for $T_{\text{ad}} = 1000$ K and $T_{\text{ad}} = 2000$ K, respectively. Here, the equivalence ratio is determined using both H_2 and TMT as fuels according to the global reaction



At stoichiometric conditions, all tin is presumed to form SnO_2 , all hydrogen to form H_2O and all carbon to form CO_2 . In order to separate temperature effects from fuel-to-oxidizer ratio effects, the results of Figs. 11 and 12 are presented for approximately constant temperatures. For all calculations, the fuel loading is maintained at one mole of TMT and one mole of H_2 , the reactants are at 1 atm and 298 K, and the reaction is considered adiabatic. The equivalence ratio is changed by increasing or decreasing the O_2 concentration (x in Reaction I). The temperature is maintained constant in the calculations by increasing or decreasing the Ar concentration in the reactants (y in Reaction I). The reactants, major products of combustion (CO , CO_2 , H_2O), some minor products of combustion (H , OH , HO_2 , O), and vapor and condensed phases for Sn, SnO and SnO_2 are considered in the calculations.

Figure 11 shows that $\text{SnO}_2(l)$ is the preferred form of tin for low equivalence ratios, whereas at fuel rich conditions, $\text{Sn}(l)$ is preferred. There is a small window in ϕ where $\text{SnO}(l)$ is present, but never in quantities above 30% (mole basis) of the initial one mole of TMT. However, as the temperature is increased, Fig. 12 shows that $\text{SnO}(g)$ is the preferred form of tin for a large range of equivalence ratios. Although the calculations are not directly representative of the synthesis system studied, the trends are in excellent qualitative agreement with the observed dependences on T and ϕ . At higher temperatures and higher fuel concentrations, the O atoms are consumed preferentially by carbon, yielding Sn and SnO products. Conversely, at lower temperatures and fuel lean conditions, 100% of the TMT is converted to SnO_2 . Again, the experimental results indicate that chemical reaction is rapid, and equilibrium product distributions can be achieved using this synthesis method. Increased proportions of SnO may be obtainable by supplying additional oxygen-scavenging carbon sources, i.e. methane, ethane, etc., in the precursor supply.

Previous flame synthesis studies of Sn or SnO have not been described in the prior art. The results of the present process can be compared on a qualitative basis with other combustion synthesis methods used to produce SnO_2 nanoparticles. It is difficult to compare results on a quantitative basis, due to the limited data available on particle residence time and temperature. Lindackers et al. examined SnO_2 synthesis using low pressures (37.5 mbar), in premixed TMT/ H_2 / O_2 /Ar flat flames. The final product powders index to the cassiterite phase of SnO_2 ; however, an intermediate metastable phase (a mixture of the high-temperature β - SnO_2 phase and the α -SnO phase) is also identified in the study. The powders consist of primary particles and agglomerates with specific surface areas ranging from ~ 70 -160 m^2/g , corresponding to average particle sizes ranging from ~ 5.5 -13 nm. Higher TMT loadings lead to larger particle sizes, and the highest TMT loading is 1348 ppm. The SnO_2 particles produced using the MEDFB are larger than those made by Lindackers et al., which is consistent with the atmospheric pressures and the higher TMT loadings, 21-23% mole basis TMT, balance Ar, employed.

Pratsinis and co-workers studied SnO_2 synthesis using atmospheric pressure co-flow diffusion flames and premixed burner-stabilized and premixed burner non-stabilized flames. For all systems, the SnO_2 particles indexed to cassiterite and were larger than those produced by the subject invention process, with particle sizes determined from specific surface areas ranging from ~52-164 nm for the diffusion flames and from ~36-65 nm for the premixed flames.

Table 2. Experimental conditions and results

Case	ϕ^a	H ₂ [lpm]	O ₂ [lpm]	Ar [lpm]	TMT/Ar [mlpm]	Sample Height, H _s [cm]	Chimney Present	Measured Production Rate [mg/s]	Powder Color ^b	Predicted Production Rate [mg/s]	T _{ad} ^a [K]
1	0.75	2.94	1.95	24.44	62.6	34	Yes	0.56	W	1.42	1410
2 ^c	0.90	2.48	1.38	17.25	395	3.2/5.2 ^c	No	—	—	8.93	1590
3 ^d	0.99	2.94	1.48	18.64	35-212 ^d	—	Yes/No ^d	—	—	variable ^d	1690
4	0.99	2.94	1.48	11.70	64.3	34	Yes	—	G/Y	1.45	2160
5	0.99	2.96	1.50	18.82	268	25	No	—	W	6.05	1690
6	1.00	2.94	1.48	18.49	80.7	34	Yes	0.30	W	1.82	1700
7	1.00	2.94	1.48	18.49	82.7	34	Yes	0.23	W	1.87	1700
8	1.00	2.94	1.48	18.49	82.7	34	Yes	0.13	W	1.87	1700
9 ^e	1.02	5.33	2.61	14.85	395	5.2 ^e	No	—	—	8.93	2430
10	1.03	2.96	1.44	18.97	86.6	21	No	0.03	W	1.96	1650
11	1.18	2.98	1.26	17.67	30.3	34	Yes	0.33	G/Y	0.69	1560
12	1.18	2.98	1.26	12.72	64.3	34	Yes	0.29	G/Y	1.45	1880

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Case	ϕ^a	H ₂ [ppm]	O ₂ [ppm]	Ar [ppm]	TMT/Ar [mlpm]	Sample Height, H _s [cm]	Chimney Present	Measured Production Rate [mg/s]	Powder Color ^b	Predicted Production Rate [mg/s]	T _{ad} ^a [K]
13	1.19	3.49	1.47	18.33	60.9	34	Yes	—	G/Y	1.38	1670
14	1.20	3.50	1.47	18.33	60.9	34	Yes	—	G/Y	1.38	1670
15	1.21	3.58	1.48	18.49	60.9	30	No	0.04	W	1.38	1660
16	1.27	3.00	1.18	13.91	82.7	21	No	0.13	G/Y	1.87	1700

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^aThe equivalence ratios and the adiabatic flame temperatures are based on the reactants of the primary flame, and do not include fuel or argon concentrations from the secondary flame.

^bW = white, G = gray, Y = yellow/brown

^cConditions used to obtain TEM samples from the secondary flame. The sampling heights were variable; however, H_s was less than 6 cm for all TEM samples.

^dConditions used to evaluate secondary flame heights.

The term “low nanosized” as used herein means particles of which greater than 50% by weight have particle sizes less than 100 nm, preferably less than 70 nm, more preferably less than 50 nm, and most preferably less than 30 nm. While some particles having a size greater than 500 nm may be expected, the
5 amount of such particles will constitute less than 20%, preferably less than 10%, and most preferably below values in the range of 1-5% by weight, each numerical value within the latter range being considered disclosed herein.

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all
10 possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.